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Improving Polyolefin's Degradation by New Synthesis of Cobalt 12- Hydroxyl Oleate Additive

S Velmurugan, AU Santhoskumar, K Palanivelu*

Dept of Plastic Technology, Central Institute of Plastic Engineering and Technology, Guindy, Chennai- 600032, India

ABSTRACT

A new additive Cobalt (Co) 12-hydroxyoleate was successfully synthesized and blended with starch their performance on the photodegraded low density polyethylene film was subjected to biodegradation in the presence of the microbes such as *asspergillusniger* and *pencilium funiculosum* isolated from a dump. Fragments occur progressively in the biodegradation of the photodegradaded films. Moreover, the biodegradation test results reveal that 24% of the material degradation at the end of 45 days. This Cobalt 12 hydroxyoleate blended with LDPE film has been exposed to abiotic and biotic environments. The abiotic degradable of the films were UV irradiated for periods of maximum within 120 hours of LDPE in different percentage before being mixed with water and organic fraction municipal solid compost were examined by infrared spectroscopy. The carbonyl peak increased with time in the abiotic environment and the oxidative degradation. In the presence of a biotic environment however, this peak decreased. At the same time there was an increase in double bonds which was related to weight loss. This mechanism is compared, on the one hand, with abiotic photooxidation, Norrish type I degradation and on the other with biotic polyolefin's degradation to produce double bond formation find out peak in FTIR. So it is prooxidante and bioactive LDPE Cobalt 12hydroxyoleate degradable simply.

Keywords: Biodegradation; Abiotic degradation ; Low-density polyethylene; Cobalt 12-hydroxy oleate

*Corresponding author

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INTRODUCTION

The solution of plastic ecological problem lies in the development of photodegradable and biodegradable polymer with controlled lifetime. The additives like transition metal, Ketones, quinones and peroxides are initiators of photo-degradation reactions in polyolefins [1-11]. High molecular weights result in a sharp decrease in solubility making them unfavorable for microbial attack because bacteria require the substrate to be assimilated through the cellular membrane and then further degraded by cellular enzymes. At least two categories of enzymes are actively involved in biological degradation of polymers: extracellular and intracellular depolymerases during degradation, exoenzymes from microorganisms break down complex polymers yielding smaller molecules of short chains, g., oligomers, dimers, and monomers, that are smaller enough to pass the semi-permeable outer bacterial membranes, [12,13] and then to be utilized as carbon and energy sources. The process is called depolymerization. When the end products are CO₂, H₂O, or CH₄, the degradation is called mineralization. It is important to note that biodeterioration and degradation of polymer substrate can rarely reach 100% and the reason is that a small portion of the polymer will be incorporated into microbial biomass, humus and other natural products dominant groups of microorganisms and the derivative pathways associated with polymer degradation are often determined by the environmental conditions. When O₂ is available, aerobic microorganisms are mostly responsible for destruction of complex materials, with microbial biomass, CO₂, and H₂O as the final products. In the study a metal carboxylate additive synthesized from Ricinoleic acid (12-hydroxyl oleic acid) mixed with low density polyethylene after the photodegraded film were subjected to the percentage of biodegradation by ASTM D 5338 standard and attacking on biotic exposure by analysis in Fourier Transform infrared spectroscopy.

MATERIAL AND METHOD

Experimental

Cobalt (II) chloride hexahydrate, sodium hydroxide, Ricinoleic acid (12 hydroxy oleic acid) were used without further purification. General purpose film grade LDPE 24FSO40 has been used to prepare films. Milli Q ultrapure water was used throughout the course of this work. Ba(OH)₂ and hydrochloric acid SQ qualigens in Fisher Scientific.

Synthesis and Preparation of Cobalt 12 hydroxyl oleate

The Cobalt12-hydroxy oleate was successfully synthesized using castor oil as the source of 12-hydroxy oleic acid. The additive synthesized consists of three functional groups namely a double bond between the 9th and 10th carbon atoms, a hydroxyl group at 12th carbon atom, and a metal carboxylate. In addition, the long alkyl chain of hydroxyl oleic acid imparts compatibility with polyolefins. The metal carboxylate acts as an activator to induce photodegradation in the polymer. Therefore, these metal carboxylate additives play multiple roles such as compatibilizer, photo/biodegradation activator and plasticizer. The structure of

the additives is given in Fig.1. The structure of the additives synthesized was confirmed using FTIR spectral analysis. The FTIR spectrum given in Fig.1 (A) reveals the stretching vibrations of carbonyl group at 1712 cm^{-1} and the absorption peak of metal carboxylate group at 1592 cm^{-1} . The absorption peaks at 2853 , 2922 cm^{-1} and at 3350 cm^{-1} shows the presence of long alkyl chain and hydroxyl groups respectively in Cobalt oleate additive. The absorption peak at 1436 cm^{-1} pertaining to carbon – carbon double bond which confirms the unsaturation in the alkyl chain of Cobalt oleate additive.

Blending and film preparation of LDPE

LDPE was blended with synthesized Cobalt 12 hydroxyl oleate in varies percentage 1%,3% and 5% by using Torque Rheometer, blending was carried out at a temperature range of $130\text{-}190^{\circ}\text{C}$ and at a screw speed of 75 rpm. Subsequently, the pellets are dried in a dehumidifier at 70°C for two hours to remove moisture. The film was prepared by using film die for all the three percentage of additive. The three percentages of additives. The wall thickness of the film was kept at 50 microns by controlling the speed of the nip rollers and output rate.

Elemental Analysis

The carbon content of the each test sample determined by elemental analysis by using Carlo Erbal model 1106 elemental analysis in table 1.

Biodegradation Test

The Cobalt oleate additive blended LDPE fragmented films after exposed to photodegradation were subjected to biodegradation test as per ASTM D 5338 for determining the aerobic bio-degradation under controlled conditions. The compost used was standard vermi compost. The reaction temperature was maintained at $58\pm 2^{\circ}\text{C}$ and the compressed air was passed at the rate of 100 ml/min . The test duration was 45 days and the reference material used was cellulose. The percentage of biodegradability was obtained by determining the percentage of carbon in the test sample that is converted into CO_2 during the biodegradation of film samples.

Experimental Details

The details of the biodegradation experiment are summarized below;

Sample detail: brittle fragmented photo-degraded LDPE/Cobalt 12 hydroxyl oleate film.

Origin of compost	: Municipal and vegetable waste
Reaction Temperature	: $58^{\circ}\text{C} (\pm 2^{\circ}\text{C})$
Dry Solid (%)	: 50
Volatile Solid (%)	: 20
Air flow rate	: 100 ml/min



Test duration (day)	: 45 days
Reference material	: Cellulose
Volume of reaction vessel	: 3000 ml
Moisture percentage in compost	: 28 %

The preparation and aging of the compost for biodegradation of film samples was carried out as per the standard. Barium Hydroxide solution (0.025 N) was prepared by dissolving 4.0 g of anhydrous barium hydroxide in 1000ml of distilled water. The solution was filtered and the normality was determined by titrating against standard acid solution and stored in a sealed container as a clear solution to prevent absorption of CO₂ from air. About 5-20 L of 0.025 N barium hydroxide solutions was prepared at a time for running a series of tests. However, care was taken that a film of BaCO₃ does not form on the surface of the solution in the glass vessels, which would inhibit CO₂ diffusion into the absorbing medium.

Procedure

The composting vessels were incubated in diffuse light minimum for a period of 45 days & the temperature of the system was maintained at 58±2 °C. The CO₂ & O₂ concentrations were checked in the outgoing air daily with a minimum time interval of 6 hrs after the first week. The air flow was adjusted to maintain a CO₂ concentration of at least 2% volume to allow accurate determination of CO₂ level in the exhaust air. Composting vessels were shaken weekly to prevent extensive channeling which could provide uniform attack of microbes on test specimen and provide an even distribution of moisture. The incubation time was fixed for 45 days.

Carbon Dioxide Analysis:

The carbon dioxide (CO₂) produced in each vessel reacted with Ba(OH)₂ and was precipitated as barium carbonate (BaCO₃). The amount of carbon dioxide produced was determined by titrating the remaining barium hydroxide with 0.05 N hydrochloric acid to a phenolphthalein end point. Because of the static incubation, the barium carbonate built up on the surface of the liquid was broken up periodically by shaking the vessel gently to ensure continued absorption of the evolved carbon dioxide. The hydroxide traps were removed and titrated before their capacity exceed. At the time of removal of the traps, the vessel was weighed to monitor moisture loss from the soil and allowed to sit open so that the air was refreshed before replacing fresh barium hydroxide and releasing the vessel. The carbon dioxide evolution rate reaches a plateau when all of the accessible carbon is oxidized. The test was terminated at this point. At the conclusion of the test, the pH and moisture and ash content of the soil is measured and recorded.

RESULTS AND DISCUSSION

Elemental Analysis

Table 1 Elemental analysis percentage of carbon, hydrogen, Nitrogen for LDPE - Cobalt 12 hydroxyl oleate

Sample	Cellulose (%)	1% LDPE (%)	3% LDPE (%)	5%LDPE (%)	Compost (%)
Carbon	84.47	86.62	84.86	85.46	14.23
Hydrogen	14.76	13.00	13.89	14.35	1.76
Nitrogen	0.17	.06	0.25	0.16	1.54

C, H and N elemental analysis reported in table below and then pure Cobalt 12-hydroxy oleate. Cobalt percentage 9.87 % as shown in Table 1. It has Carbon, Hydrogen and Nitrogen analysis only. Carbon values of cellulose dependent carbon and hydrogen analysis only independent of the oxygen in molecular structure.

Biodegradation of the LDPE with Cobalt 12 hydroxyl oleate

According to reference [14] ASTM D 5338 conditions of reaction mixtures: Organ of compost; livestock excrement, municipal and Vegetable waste used the method used for the determination of the biodegradability of the polyolefin's was based on the International Standard (ASTM 5338-98) that measures the evolved CO₂ amount from both the blank vessel without a sample and the sample vessel including a 10 g LDPE Cobalt 12-hydroxyl oleate samples. According to the experimental 2.7 ASTM 5338 test procedure. Polyethylene the percentage of biodegradation 24 % in Fig.2

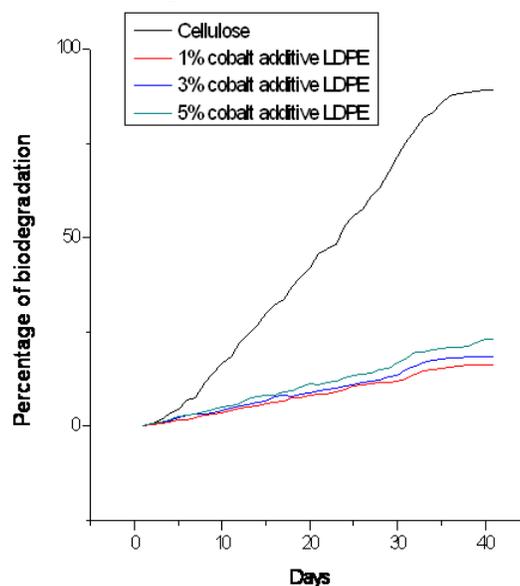


Fig.2 Bio-degradation curve for the photodegradable product of LDPE 1%, 3 % and 5% film.

Reaction temperature : 58±2°C
 Dry solid (%) : 52%
 Volatile solid (%) : 19%

Air flow rat	:	100 ml/min
Test duration (day)	:	45 day
Reference material	:	Cellulose
Volume of reaction vessel	:	2000ml
Moisture percentage in compost	:	28 %
PH before and after biodegradation:		7.6 to 7.9

Fourier Transform Infrared Spectrophotometer (FTIR)

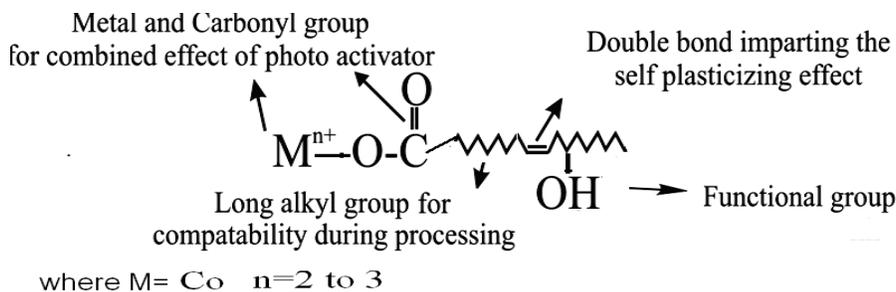


Fig.1 Generally structure of Cobalt 12- hydroxyl oleate

Fig.1 showing the new class of generally structure of Cobalt 12- hydroxy oleate used for a study of the IR spectra of biotically degraded LDPE. It was observed that the carbonyl index decreased with prolonged incubation time after the effect of UV exposure LDPE-Cobalt 12 hydroxyl oleate for fifth days. In fig.3 (D, E & F) the explanation for this is given by the mechanism in some IR spectra of biotically degraded LDPE was noted corresponding to double bond groups 1634 cm⁻¹ in the additive. In fig 3 (C) this peak was missing in abiotic (photo degradation) samples.

Differentiate FTIR spectra for virgin LDPE compared to biotically degraded film from the photodegraded films. The photodegraded films or Before biodegradation typical FTIR spectra as shown in Fig.3 (C) and the measurement of carbonyl index 1712 cm⁻¹, the conventional spectroscopic monitor of polymer degradation were made by measuring the IR transmission spectral of film after exposure for increasing lengths of time in QUV accelerated weathering equipment fitted with UVA -340 tubes and operated at 60 ° C the broad band radiation from the UVA-340 tubes has been shown to emulate sunlight in the wavelength range below 360 nm. The development of carbonyl groups was monitored and the carbonyl index, the absorbance at around 1712 cm⁻¹ was recorded. (As the film used in this study were 50 μ thickness, the carbonyl index is numerically equivalent to the absorbance). Reference [15] is frequently made to Cobalt 12 hydroxy oleate films degradation by microorganisms when LDPE its instability towards environmental factors are discussed.

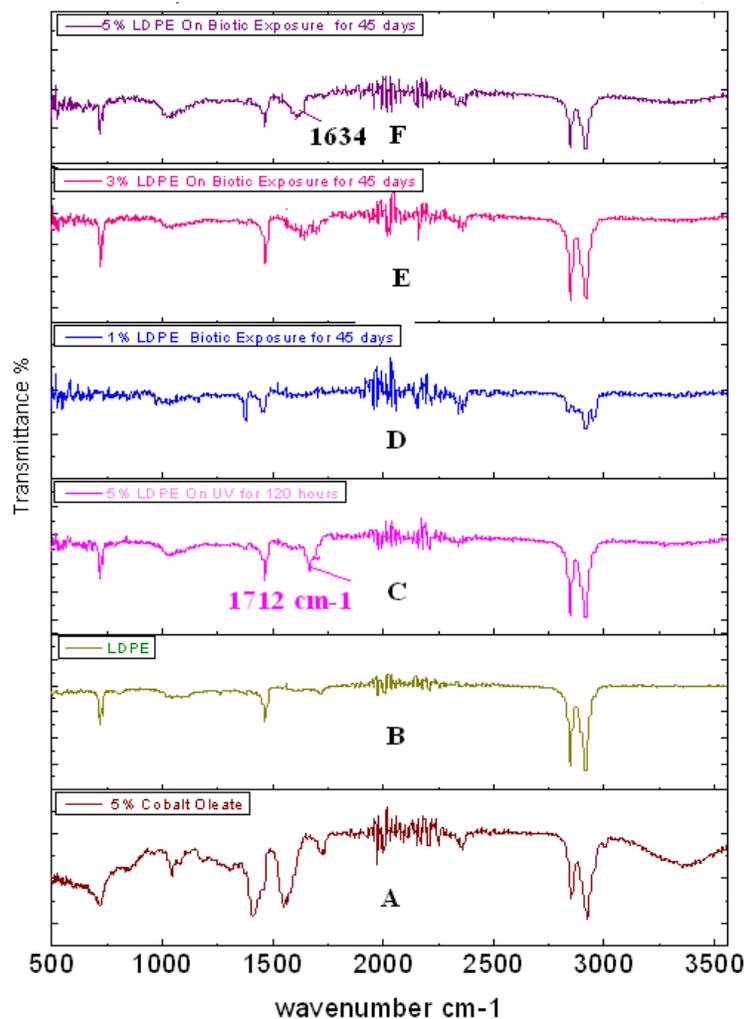


Fig.3 Characteristic peak in FTIR for Cobalt 12 hydroxyl oleate (A) Characterization peak in FTIR for virgin pure LDPE (B), Characterisation peak in FTIR for LDPE 1, 3, 5% Cobalt 12 hydroxyl oleate after Biodegradation C=O increases 1712 cm^{-1} , Characterisation peak in FTIR for LDPE 1, 3, 5% Cobalt 12 hydroxyl oleate after Biodegradation -C=C- slightly increases 1634 cm^{-1}

This is fairly understandable since a Cobalt 12 hydroxyl oleate can be classified as a very short-chain LDPE, The length of typical Cobalt 12 hydroxyl oleate, being 10-20 carbons chains. Microorganisms preferentially use linear carbon chain, whereas the corresponding branched isomers are almost completely inert to biodegradation. Fig.4 the mechanism for degradation of Cobalt 12 hydroxy oleate by microorganisms responsible for the attack on Cobalt 12 hydroxy oleate can be, for example, *Aspergillus Niger* and *Penicillium funiculosum*. The polyethylene is oxidized to a carboxylic acid and the resultant acid undergoes β -oxidation which, by reaction with coenzyme A, removes two carbon fragments from the carboxylic molecule. The two carbon fragments, acetyl-S-CoA, enter the citric acid cycle, from which carbon dioxide and water are released. From a Cobalt 12 hydroxyl oleate molecule with n carbons, a total of n molecule of carbon dioxide evolved [15]. Fig.3 shows the virgin LDPE samples to be analyzed by IR were cut out from the films. In the IR spectra, special interest was focused on

the following absorption peak: 729 cm^{-1} , rocking vibration ($-\text{CH}_2-$); 1376 anti symmetric deformation($-\text{CH}_3-$); 1470 cm^{-1} symmetric deformation ($-\text{CH}_2-$); 1604 cm^{-1} , Symmetric deformation($-\text{CH}_3-$); 2913 anti symmetric deformation($-\text{CH}-$); 2847 symmetric stretching($-\text{CH}_3-$).

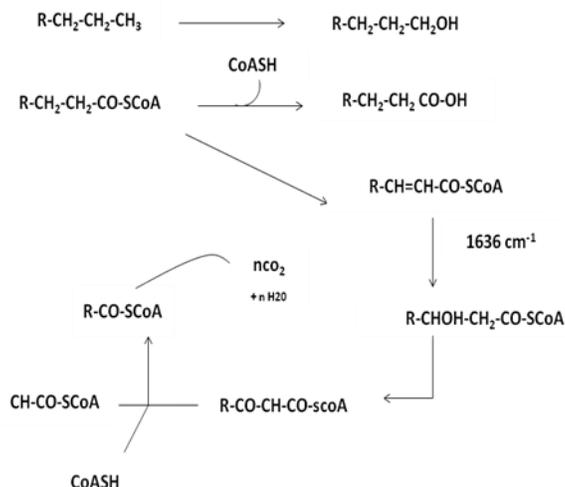


Fig.4 Biotic Paraffin Degradation Mechanism to H.G schlagel (1976),

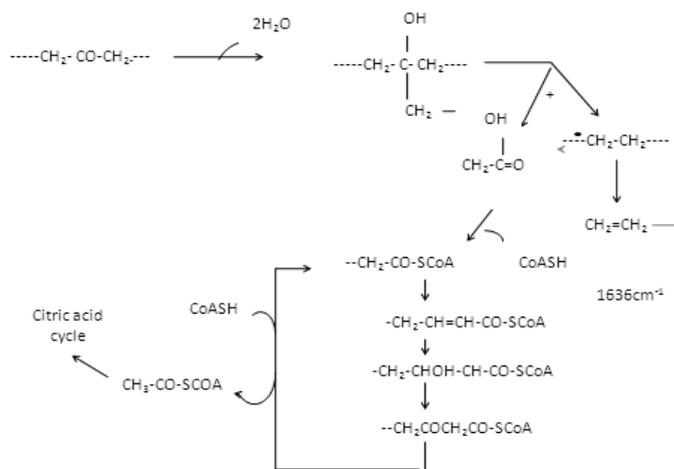


Fig. 5 Proposed mechanisms for the biodegradation of polyethylene

A proposed mechanism for the biodegradation of LDPE is given in Fig.5 it is thought that the alteration of LDPE molecule is initially the same in both the abiotic (photodegradation) and biotic samples. When carbonyl groups had been formed, the abiotic sample evidently did not undergo Norrish type II degradation as no double bond peak could be found in the IR spectra from abiotically (photodegradation) degraded LDPE fig.3 (C). According to the figure 3 (C), the carbonyl index increased with prolonged incubation in an abiotic atmosphere. Alkenes formation had, however taken place, as was confirmed by the presence of peaks at 1634 cm^{-1} in biologically affected films



CONCLUSION

The rate of the new additive Cobalt (Co) 12-hydroxyoleate was successfully synthesized and their performance on the photodegraded low density film was subjected to biodegradation of LDPE is very high at higher concentration of Cobalt 12 hydroxyl oleate. After the biotic exposure in the FTIR analysis shows that a peak at around 1634 cm^{-1} corresponding to double bond group of transition metal 12-hydroxyl oleate was observed for LDPE films with up to 5%. The biotically degraded product when subject to biodegradation has results in 24% of LDPE biodegradation in 45 days. So, Cobalt 12 hydroxyl oleate is used as an effective biodegradable additive for LDPE films.

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